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Author(s): Luther, Erik Paul  
Leckie, Rafael M.  
Dombrowski, David E.  
Papin, Pallas A.

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# Fabrication of TREAT Fuel with Increased Graphite Loading

Erik Luther, Rafael Leckie, David Dombrowski, Pallas Papin

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## Summary

As part of the feasibility study exploring the replacement of the HEU fuel core of the TREAT reactor at Idaho National Laboratory with LEU fuel, this study demonstrates that it is possible to increase the graphite content of extruded fuel by reformulation. The extrusion process was used to fabricate the “upgrade” core<sup>1</sup> for the TREAT reactor. The graphite content achieved is determined by calculation and has not been measured by any analytical method. In conjunction, a technique, Raman Spectroscopy, has been investigated for measuring the graphite content. This method shows some promise in differentiating between carbon and graphite; however, standards that would allow the technique to be calibrated to quantify the graphite concentration have yet to be fabricated. Continued research into Raman Spectroscopy is on going. As part of this study, cracking of graphite extrusions due to volatile evolution during heat treatment has been largely eliminated. Continued research to optimize this extrusion method is required.

## Introduction

The Department of Energy (DOE) is proposing to re-establish the capability to conduct transient testing of nuclear fuels. Candidates for transient testing are The Transient Reactor Test Facility (TREAT) reactor at Idaho National Laboratory (INL) and the Annular Core Research Reactor (ACRR) at Sandia National Laboratories (SNL). Currently, the DOE has not made a decision about whether to conduct transient testing at either facility; however, the National Nuclear Security Administration (NNSA) Global Threat Reduction Initiative’s Reactor Conversion Program is supporting reactor conversion fuel studies to convert the TREAT reactor from its existing highly enriched uranium (HEU) core to a new core containing low-enriched uranium (LEU).

In support of this objective, computational modeling and analysis efforts are currently being performed. Those studies have revealed that maximizing the graphite content of the LEU fuel assemblies may have a significant positive impact on reactor performance. Those studies are on-going but have spurred an interest in studying fabrication methods that maximize the graphite content of the fuel. This report documents efforts to modify the existing extrusion fuel fabrication methodology to maximize graphite. In conjunction, this study has investigated RAMAN spectroscopy as a method of quantifying the graphite content of extruded fuel. This report also documents efforts to minimize cracking that has been identified in extruded fuels.

## Technical Approach

### Raw Materials

For the original upgrade fuel fabrication, the raw materials for the fuel elements consisted of graphite flour (grade S97 from Airco-Speer Carbon Company, St. Mary's, PA), carbon black (Thermax) and Varcum resin, a partially polymerized furfuryl alcohol. Uranium oxide ( $\text{UO}_2$ ) was synthesized at LANL for the upgrade core.

An earlier search for these feedstocks revealed that neither the graphite flour nor Varcum resin are available. The original grade of Thermax is no longer available as the company has changed hands. Uranium oxide is no longer produced in significant quantities at LANL although small scale batches can be synthesized.

For this study, legacy S97 graphite flour and Thermax carbon black were located in large quantities sufficient for significant testing and even pilot scale production. Legacy depleted uranium oxide ( $\text{UO}_2$ ) produced at LANL for TREAT fabrication studies was also located in relatively large quantities. Two varcum type resins (Quacorr 1001, Penn A Kem and Durez 29577, Durez Corporation) as well as partially polymerized furfuryl alcohol were used in this study.

Furfuryl alcohol was prepolymerized with maleic anhydride as described in earlier reports<sup>2</sup>. In order to catalyze polymerization for all of the resins, prior to extrusion, 10 parts by mass of maleic anhydride dissolved in acetone (50 wt%/50 wt%) was added to 100 parts resin and shaken to initiate the final cure.

For most extrusions, carbon was eliminated from the composition and replaced with graphite. Because the carbon has a significantly finer particle size distribution than any of the graphites available, the graphite was milled and sieved.

The particle size distributions of carbon and graphite are shown in Figure 1. As received carbon is significantly narrower and finer particle size than as received graphite. By milling and sieving the graphite through 400 mesh, the particle size distribution is shifted finer and narrower; however, it is still about an order of magnitude larger than the carbon.

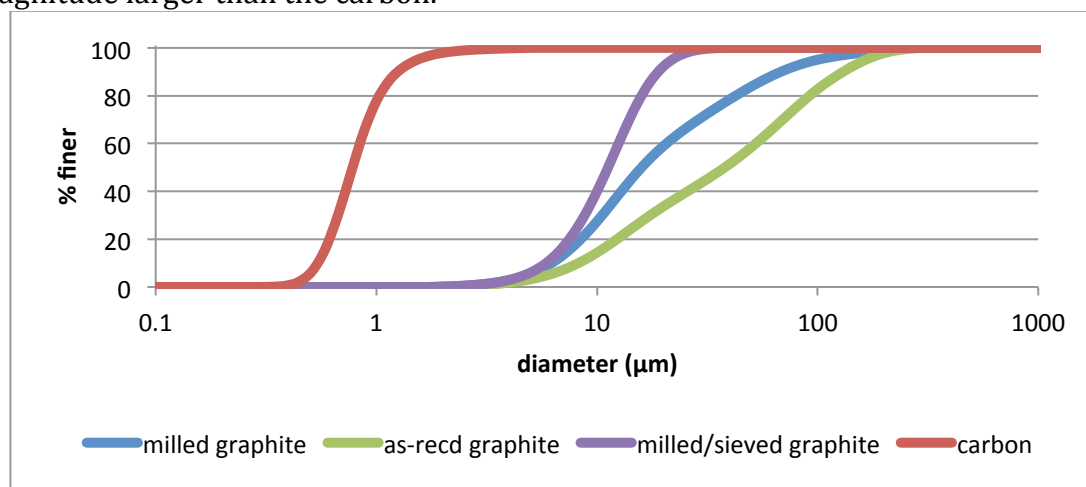


Figure 1 Particle size analysis of powder feedstocks used in the fabrication of TREAT fuel.

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Replacing the carbon with milled graphite tended to increase the resin concentration required for extrusion; however, it is known that the final optimized composition used for fabrication will depend greatly on details of the production extruder. For instance, the reduction ratio in production will be significantly greater ( $>7:1$ ) relative to that used in these fabrication studies ( $\sim 2.7:1$ ). This will have the effect of greatly increasing the extrusion tonnage and likely reducing the resin required. Also, the exact resin used and its viscosity will certainly affect the quantity needed. Furthermore, it is likely that the die will be heated. Table 1 shows the baseline composition along with an approximate resin addition. As seen in the table, most of the trial extrusions were made without uranium oxide. The amount of resin was varied significantly to explore the processing space. In most cases, more resin was added to compensate for the larger average particle size but in at least one case, a good extrusion was accomplished with a minimal amount of resin.

Table I Composition of fuel extrusion mixes		
	Baseline (grams)	Milled graphite (grams)
Uranium oxide	25.4	0
Graphite	404.4	404.4 unmilled/82.8 milled
Carbon	82.8	0
Resin	247 to 267	309 to 372

The graphite content of these extrusions may be calculated assuming that neither carbon nor resin converts to graphite during any of the heat treatments. Since the highest temperature these heat treatments have been exposed to is  $1250^{\circ}\text{C}$  and the acknowledged graphitization temperature exceeds  $1700^{\circ}\text{C}$ , this is a reasonable assumption. Thermogravimetric Analysis (TGA) shows that the resin loses approximately 77.3 wt% volatiles upon heating. The remaining material is presumably converted to carbon. For the baseline composition, the graphite content varies from 56.2 wt% to 57.5 wt%. For the all graphite composition the content varies from 62.9 wt% to 67.1 wt%. In these calculations, one factor that cannot be accounted for is the percentage of volatile evolution of the resin. It is known that there is a significant portion of small chain hydrocarbons that will evolve during the heat treatment process as evidenced by deposits in the heat treatment furnaces. As a result, the calculations will underestimate the graphite content in the extrusions.

### Raman Spectroscopy

Due to the uncertainty associated with calculations to determine the graphite content of extrusions, a characterization method capable of distinguishing between amorphous carbon and graphite was sought. There are three difficult challenges with this task: First, there is no chemical difference between the materials; Second, although many techniques can identify amorphous materials, few, if any can quantify them; Third, the technique must be a bulk method.

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Discussions with several characterization experts suggested that diffraction techniques were unlikely to help. Both X-ray and neutron diffraction would see amorphous phases as large broad humps in the diffraction pattern but methods to quantify the phase are lacking. Raman spectroscopy was suggested as a possible alternative. Raman would likely see both carbon and graphite; however, creating standards and identifying factors that affect the signal were challenges. As a result, several samples were scanned by Raman to try to understand some of these factors.

Figure 2 shows the Raman scans of the raw materials carbon and graphite. The scans are easily differentiated with graphite showing some distinct peaks. Figure 3 compares the graphite raw material with heat treated extrusions with and without carbon. While there are clear differences between the extrusions with and without carbon, it is not immediately obvious how to interpret the signals. A series of extrusions with varying amounts of carbon is being prepared to study this effect.

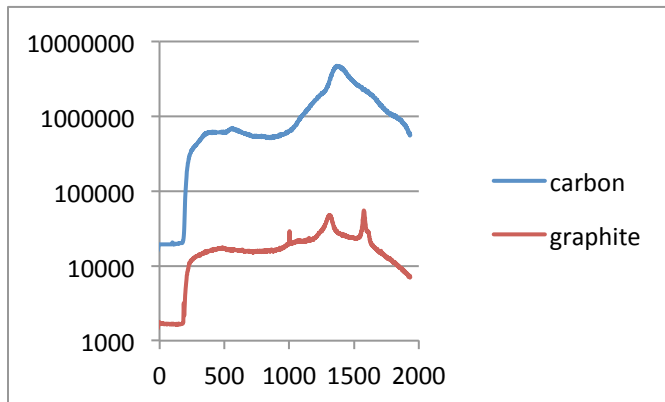


Figure 2 Raman spectroscopy of carbon and graphite.

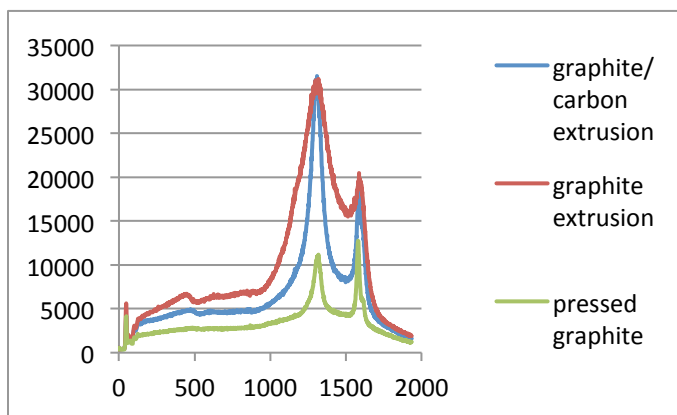


Figure 3 Raman spectroscopy of extrusions compared with graphite feedstock.

### Cracking

Extrusions made for the TREAT fuel fabrication studies have consistently cracked during initial heat treatments. The cause of the cracking is clearly traced to the evolution of volatile species from the resin. These volatiles do not have an escape path and cause cracks and bloating in the samples. Even heating rates as low as 1°C/hour (as low as practical for any type of production) have not allowed sufficient time for volatile escape. This was discussed in a previous report. In this study, several options were attempted to minimize or eliminate cracking. With the slowest heating rates, a typical cracked microstructure from a graphite/carbon extrusion is seen in Figure 4. In Figure 5, the microstructure of an all graphite extrusion is seen. Cracking is similar in these images therefore the switch to all graphite extrusions was concluded to not be a contributor to cracking. In all of the



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following tests (except the flash heating), the extrusions are all graphite and the heating rates were kept the same.

#### Elimination of Volatiles

In an attempt to remove volatiles prior to the extrusion, both commercial resin and partially polymerized furfuryl resin were subjected to heat or vacuum prior to mixing with the powder feedstocks. It was expected that the lowest vapor pressure species would readily evaporate minimizing the volume of volatiles that must escape during the heat treatment.

Even in the best cases, evacuation of the resin overnight was found to remove only about 1.5 wt% while heating for 5 hours at 60°C removed about 4.5 wt%. Even using both procedures prior to extrusion resulted in no improvement in cracking.

#### Commercial Resins

It was speculated that resins from commercial sources might contain less volatiles than the partially polymerized furfuryl alcohol prepared using LANL procedures. Subsequently, resins from Penn A Kem (Quacorr 1001) and Durez Corporation (Durez 29577) were identified and procured. Both resins are varcum/furan types meaning that they are partially polymerized furfuryl alcohols; however, details of the curing process are not known and this could have significant influence on volatile evolution. All graphite extrusions using both resins were prepared. Figure 6 shows an image of the cracking seen in an extrusion made using the Quacorr resin. Cracking was unexpectedly extensive. Cracking in extrusions made from Durez were similar. As a result, subsequent extrusions were made using the LANL prepolymerized furfuryl alcohol.

One positive outcome from these experiments was the realization that the

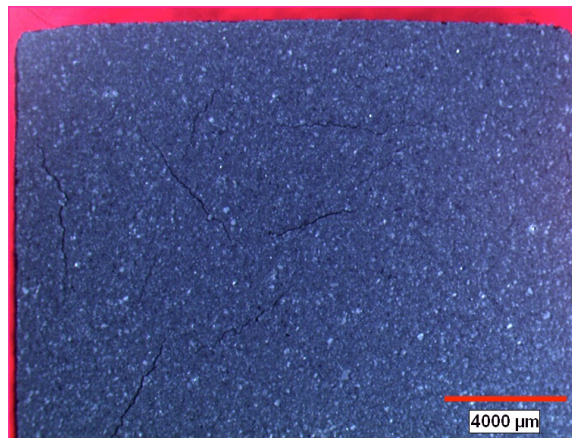


Figure 4 Cracking seen in baseline graphite/carbon extrusion.

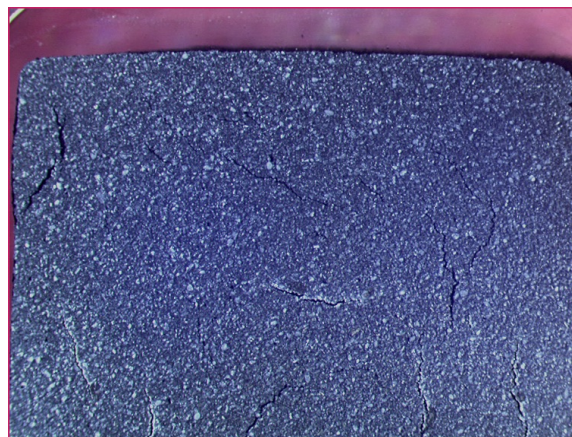


Figure 5 Cracking seen in all graphite extrusion.

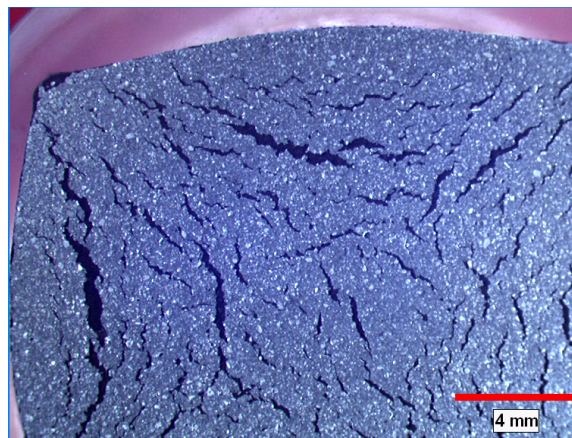


Figure 6 Extrusion made with Quacorr resin.

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volatile of concern; i.e., causing the most cracking, was likely water which is a product of the resin curing which occurs after extrusion. As a result, elimination of volatiles prior to extrusion was no longer considered necessary.

### Full Cure

It was speculated that the amount of volatiles evolved would be less if the resin was allowed to cure fully prior to heat treatment. It was also felt that the samples might dry in Los Alamos' low humidity climate. A sample of an extrusion that was allowed to cure for a full month was heat treated. This sample is seen in Figure 7. Qualitatively, cracking appears to be more severe so this approach was not pursued.

### Flash Heating

While counter intuitive, it was speculated that a rapid heat treatment might quickly eliminate volatiles on the surface of the extrusions leaving porosity. This porosity might provide a path for elimination of volatiles within the sample. Samples were pushed into hot furnaces at 70°C, 150°C, 200°C and 250°C and left for half an hour at temperature. In all cases, samples were cracked and in most cases they were severely bloated. Figure 8 shows a sample flash heated to 250°C. This sample fared the best although large cracks are still observed.

### Wood Flour

Knowing that a path for volatile escape was needed to prevent trapped gases from cracking the samples, wood flour was added to the composition. Wood flour has been added to graphite compositions for this purpose in the past because it readily chars leaving only carbon behind but adds porosity in a controlled manner. Approximately 15 wt% wood flour was added to this mixture on a dry basis. That amount dropped to about 7 wt% after adding resin. An unexpected outcome was that significantly more resin had to be added to the mix in order to achieve an

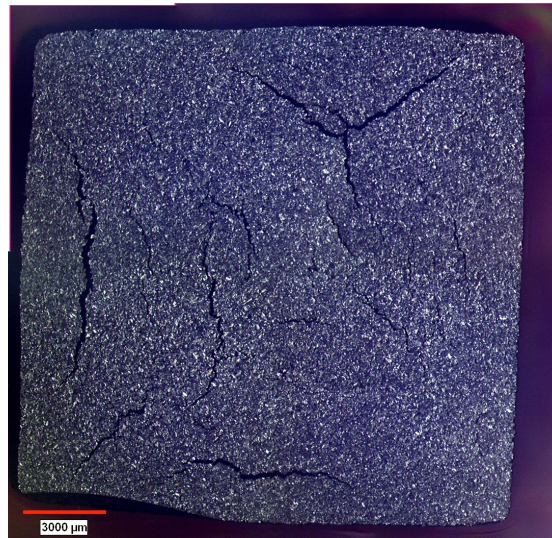


Figure 7 Cracking in an extrusion heat treated after a full one month cure.



Figure 8 Cracking in a sample flash heated to 250°C.



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extrudable mass; an increase from 33 wt% to 47wt% resin. Figure 9 shows the cracking found in this sample. Due to the extensive cracking and the decrease in overall graphite content caused by the increased resin and wood flour, this approach was thought to be unproductive.

### Vacuum Heat Treatment

Although counterintuitive at first glance, the standard heat treatment was attempted under vacuum as opposed to air. While the vacuum will cause the volatiles to gasify more readily, it was also expected that they would come out earlier in the heat treatment. Two samples were subjected to the vacuum heat treatment. In Figure 10 shows an all graphite extrusion that has been subjected to the vacuum heat treatment. Although porosity is severe, it was noted that cracks were not as clearly present. This approach might have been abandoned altogether; however a sample containing wood flour was also part of this heat treatment. Figure 11 shows the microstructure. Remarkably, the wood flour has provided an escape path for volatiles as the sample is nearly crack free.

## Conclusions

This study has demonstrated that it is feasible to increase the graphite content of fuel fabricated for the TREAT program by extrusion; the “upgrade” fuel process. This is accomplished by reformulating the extrusion mix with milled graphite replacing carbon. The actual graphite content is determined by calculation and has not been measured by any analytical method. A technique that has been investigated for measuring the graphite content is Raman Spectroscopy. This method shows some promise in differentiating between carbon and graphite; however, it is early in the study and standards that would allow the technique to be calibrated to quantify the graphite concentration have not been fabricated. Continued research in this area is recommended. Cracking of graphite extrusions due to volatile evolution during heat

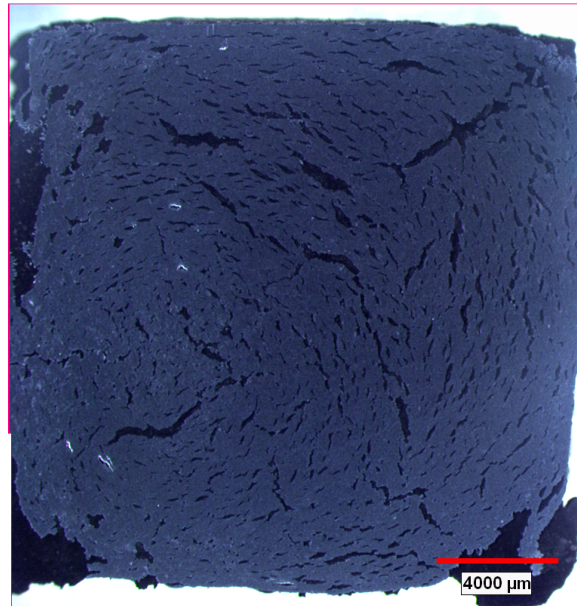


Figure 9 Extrusion containing wood flour.



Figure 10 Porosity seen in an all graphite extrusion heat treated under vacuum.



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treatment has been largely eliminated. A path for eliminating cracking has been identified; namely addition of wood flour (or some other pore former) and vacuum heat treatment. Although this method has not been optimized, initial results are promising. The drawback to this approach may be a reduction in the total graphite content due to the addition of wood flour and additional resin both of which convert to carbon upon heat treatment.

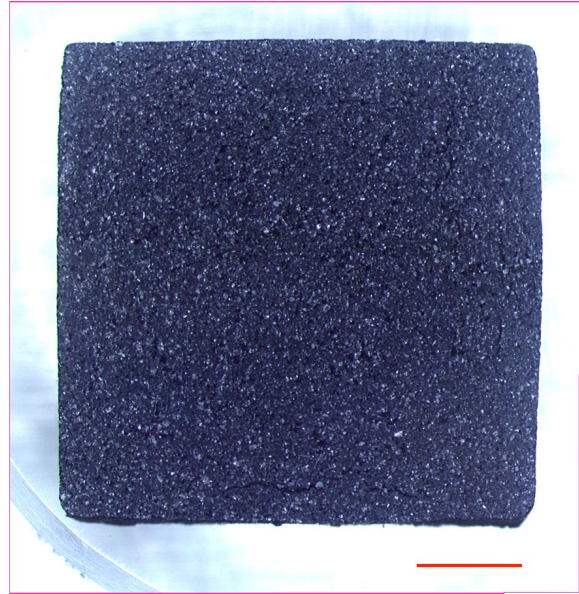


Figure 11 Nearly crack free extrusion of graphite and wood flour heat treated under vacuum.

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<sup>1</sup> K.V. Davidson, D.H. Schell, "TREAT Upgrade Fuel Fabrication, LANL, LA-UR-79-821, CONF-790625-2.

<sup>2</sup> E Luther, C Chen, D Dombrowski, J Kennison, P Papin, D Guidry, J Hunter, "Fuel Fabrication Study for TREAT Conversion Fuel", LANL Report, LAUR-13-72850, 2013.